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On the theory of evolution of particulate systems

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Abstract. An analytical method for the description of particulate systems at sufficiently long times is developed. This method allows us to obtain very simple analytical expressions for the particle distribution function. The method under consideration can be applied to a number of practically important problems including evaporation of a polydisperse mist, dissolution of dispersed solids, combustion of dispersed propellants, physical and chemical transformation of powders and phase transitions in metastable materials.

1. Introduction

The most simple evolution problems for a particulate assemblage arise in numerous processes where 1) there is no exchange by particles between the assemblage and external forces, 2) new particles do not originate, and 3) fluctuations in the transformation rate of a single particle are negligible. Such processes are wide-spread in multifarious fields of modern technology, and they range from basically unsophisticated processes, in which particles either increase or decrease their size due to heat and mass exchange with their environment, to much more complicated conversion processes, such as combustion of pulverized propellants or chemical transformation of powders.

A significant common feature of such processes consists in the fact that all of them can be described with the help of the simplest possible version of the Fokker-Planck evolutionary equation which does not include 1) terms involving second derivatives of the population density distribution function, and 2) any source terms. Even though, dealing with such an equation presents essential difficulties, and evaluation of the distribution function and various properties of the particulate assemblage and its environment at different moments of time usually entrails a great deal of cumbersome and tedious numerical calculations.

An alternative method is advanced in this paper which allows us to get very simple analytical results for the particle distribution function at sufficiently long times having elapsed after the beginning of an evolution process. This method was successfully applied to a number of practically important problems (see, among others, [1–3]). It is based on introducing a set of self-similar functions that exponentially decrease in amplitude, but do not change their shape, during the process. The distribution function can be represented as a sum of such self-similar functions. At long times, only the term with a minimal rate of change remains, whereas other terms eventually degenerate. From the physical point of view, this means that the particulate assemblage forgets particulars of its initial distribution as time goes by, and only its relatively rough features endure.

2. The essence of the method

Let us consider an assemblage of particles that are continuously distributed over some physical character designated by the parameter ξ. Most commonly, parameter ξ characterizes particle size; but it can also to have other physical meaning, such as a degree of physical transformation or chemical conversion of particles. At any moment of time, the current distribution of the assemblage over this parameter can be described with the help of the particle population density distribution function, $f(t, \mathbf{r}; \xi)$, which is regarded as normalized to the number concentration, $n(t, \mathbf{r})$, of particles.

2.1. General formulation

Under the assumptions enumerated in the beginning of this paper, the evolution of the distribution function over time and in space is governed by a first-order kinetic equation

$$\frac{\partial f}{\partial t} + \nabla \cdot (\mathbf{v} f) + \frac{\partial}{\partial \xi}(w f) = 0, \; w = \frac{d\xi}{dt}. \tag{1}$$

This equation represents perhaps the simplest version of the general Fokker-Planck equation. Quantity w is understood as a deterministic rate of transformation of a single particle that induces a change in parameter ξ. It is presumed known as a function of ξ, and it is also dependent on time and coordinates (either explicitly or, more often implicitly, though some other functions of t and $\mathbf{r}$). In addition, we assume that this transformation rate is expressible as a product of two separate functions separately depending on ξ and on t, $\mathbf{r}$, that is,

$$w \equiv w(t, \mathbf{x}; \xi) = -M(t, \mathbf{x}) N(\xi). \tag{2}$$

This equation actually covers a great variety of possible applications (see, among others, [4]). Exact forms of the functions in this equation are dictated by the very nature of the transformation process under study and by the kinetic peculiarities of this process. Function M usually depends implicitly on its argument, through certain variables that are employed to describe the current instantaneous state of the ambient medium into which the particles are submerged. The role of such variables is commonly played by the medium temperature, $T(t, \mathbf{r})$, and by concentrations $c_j(t, \mathbf{r})$ of various admixtures and reagents that affect particle transformation. It is significant that all such variables depend on moments of the particle distribution function, and this mere fact gives rise to a strongly nonlinear feedback between the current states of the ambient medium and the particulate assemblage itself. It is fairly well evident that equation (1) must be supplemented with equations for these variables which ultimately stem from the mass and energy conservation laws. As a symbolic representative of such equations, we formulate an equation

$$\frac{\partial c_j}{\partial t} + \nabla \cdot (\mathbf{v} c_j) = \eta_j \int w(t, \mathbf{x}; \xi) f(t, \mathbf{x}; \xi) \chi_j(\xi) d\xi. \tag{3}$$

The integration is performed here over the whole range of allowable values of ξ. In this equation, η_j is a coefficient, and χ_j is a weight function, whose exact forms are determined by the physical essence of the transformation process. The term on the right-hand side of equation (3) describes an effective source of quantity c_j per unit volume that is caused by the transformation. It is significant that more than one equation of the type of (3) may be relevant for the transformation problem under study. For instance, there are equations for temperature and vapour concentration that influence the evaporation kinetics for a polydisperse mist.

Imposing initial conditions

$$f(0, \mathbf{x}; \xi) = f_0(\mathbf{x}; \xi), \; \int f_0(\mathbf{x}; \xi) d\xi = n_0(\mathbf{x}), \; c_j(0, \mathbf{x}) = c_{0j}(\mathbf{x}) \tag{4}$$

brings to an end the formation of an initial value problem for equations (1) and (3). It is worth noting that the wanted solution to these equations can also be subjected to conditions at a certain surface $\mathbf{r} = \mathbf{r}_0(t)$, instead of initial conditions at $t = 0$.

2.2. Self-similar distribution functions

When taking into account the fact that the rate of transformation, w, is expressed in accordance with equation (2), and also using the Fourier method of separating variables, we look for elementary solutions to kinetic equation (1), so that the full solution takes the form

$$f(t, \mathbf{x}; \xi) = \mathbf{S}\left\{F(t, \mathbf{x}; s)R(\xi; s)\right\}, \tag{5}$$

where s is proportional to a separation variable, and symbol $\mathbf{S}\{...\}$ denotes either summation or integration over s. Equation (1) then splits into two equations

$$\frac{dF}{dt} + \nabla \cdot (\mathbf{v}F) + 2sMF = 0, \ \frac{d}{d\xi}(NR) + 2sR = 0, \tag{6}$$

where $2s$ being understood as a separation variable, while equation (4) reduces to

$$\frac{\partial c_j}{\partial t} + \nabla \cdot (\mathbf{v}c_j) = \eta_j \mathbf{S}\left\{F(t, \mathbf{x}; s)M(t, \mathbf{x}) \int N(\xi)R(\xi; s)\chi_j(\xi)d\xi\right\}. \tag{7}$$

An initial condition for c_j preserves its original form as written down in equation (4). To formulate an initial condition for unknown functions $F(t, \mathbf{r}; s)$, we represent the initial population density in the same manner as that used in equation (5), that is,

$$f_0(\mathbf{x}; \xi) = \mathbf{S}\left\{F_0(\mathbf{x}; s)R(\xi; s)\right\}. \tag{8}$$

Hence it becomes obvious that we are free to take, without loss in generality,

$$F_0(0, \mathbf{x}; s) = F_0(\mathbf{x}; s) \tag{9}$$

provided that functions $R(\xi; s)$are normalized in an appropriate manner (say, to unity).

Thus the main benefit of using the Fourier method consists in the fact that the problem of finding elementary distribution functions $R(\xi; s)$ becomes completely separated from the problem of determining variations of the particle population density in space and time. In its turn, the latter problem involves only integrals of the elementary distribution functions over ξ that appear in equation (7), but it by no means includes these functions themselves. Neither the aforementioned elementary functions, nor their moments, depend on time, and consequently, these functions can be properly termed as "self-similar distribution functions".

2.3. Systems of ideal mixing

Other statements of initial conditions are possible as well. For example, in order to provide for high transformation rates, a fluid medium containing suspended particles is often subjected to vigorous mixing, so that different parts of the fluid-particle system are more or less at the same conditions. In systems with ideal mixing in which the spatial dependence of all variables disappears by definition, it may be more convenient to require functions $F_0(\mathbf{x}; s) \equiv F_0(s)$ to equal unity for any s. Then, functions $R(\xi, s)$ must be uniquely determined by the initial population density, $f_0(\mathbf{x}, \xi) \equiv f_0(\xi)$. In what follows, we shall use this alternative statement of initial conditions, instead of that in equation (9),

$$F(0) = F_0(s) = 1, \text{ and } f_0(\xi) = \mathbf{S}\left\{R(\xi; s)\right\}. \tag{10}$$

A general solution to the equation (6) reads

$$R(\xi;s)=\frac{C(s)}{N(\xi)}\exp\left(-2s\int\limits_{\xi_0}^{\xi}\frac{d\xi}{N(\xi)}\right), \tag{11}$$

where $C(s)$ being looked upon as a given function of s. The relevant solution to the first equation (6) that satisfies condition (10) is

$$F(t)=\exp\left(-2s\int\limits_{0}^{t}M(t)dt\right). \tag{12}$$

Equations (11) aand (12) completely determine the wanted population density. Indeed, using them in equations (8), or (10), and (5) results in two final formulae

$$N(\xi)f_0(\xi)=\mathbf{S}\left\{C(s)\exp\left(-2s\int\limits_{\xi_0}^{\xi}\frac{d\xi}{N(\xi)}\right)\right\}, \tag{13}$$

which determines $C(s)$, if a factor of $N(\xi)$ in equation (2) for the transformation rate and initial population density $f_0(\xi)$ is known, and

$$N(\xi)f(t;\xi)=\mathbf{S}\left\{C(s)\exp\left(-2s\int\limits_{0}^{t}M(t)dt\right)\exp\left(-2s\int\limits_{\xi_0}^{\xi}\frac{d\xi}{N(\xi)}\right)\right\}, \tag{14}$$

which describes the particle population density at subsequent moments of time. Thus, equation (14) gives the generalized solution of the problem under study for systems of ideal mixing, if a factor of $M(t)$ that is involved in equation (2) is also known.

It follows from equation (13) that $C(s)$ may be regarded as known quantity, as far as initial population density and function $N(\xi)$ that appear in the left-hand side of this equation are definite. There are two major possibilities. The first possibility matches the case where the initial population density is approximated as a sum of suitable functions of the type of (11), each of which is characterized by its own value of s. In this case, corresponding values of $C(s)$ represent approximation coefficients that must be presumed known, by their very definition.

The other major possibility fits the situation where the left-hand side of equation (13) is expressed as an integral of the function that appears within the curly brackets over a certain continuous range of variable s. In such a situation, equation (13) actually represents an integral transform that relates the said function with known product $N(\xi)f_0(\xi)$. In this case, the task of finding $C(s)$ is in fact reduced to finding an integral transform that is inverse with respect to the transform mentioned. Some examples of application of this technique are presented in the following sections of this paper.

Meanwhile, it is worth noting an important feature of the population distribution densities. For definiteness, let us assume that $N(\xi)$ is always positive. Then $F(t)$ may be either positive or negative, depending on the physical nature of an evolution process under study. The integral of positive $M(t)$ over time that is involved in equation (14) is commonly a monotonously increasing function of time. If the initial particle population density has been approximated in accordance with equation (13), as a sum of a few terms corresponding to different values of s, only the term that is related to the smallest value of s is likely to prevail at sufficiently large times in the analogous sum that appears in equation (14). This means that the particle population density

can be more or less accurately approximated at large times by this term taken alone, whereas the influence of other terms eventually vanishes. If $M(t)$ is negative, only the term involving the large value of s is essential at long times, and the behaviour of the population density is in a sense opposite to that described above for the case of positive $M(t)$.

3. Evaporation of a polydisperse mist

Evolution of an assemblage of suspended droplets is governed by heat and mass exchange of the droplets with the suspending gaseous mixture. Two main limiting cases are to be singled out. The first one concerns slow evaporation under roughly isothermal conditions in a relatively cool gas. In this case, the evaporation kinetics is dictated by the rate with which vapour is removed away from the surfaces of evaporating droplets, whereas heat transfer does not play a significant role. This case is characteristic of most natural evaporation processes occurring in fogs and clouds. In the opposite limiting case, the evaporation kinetics is limited by the rate with which heat is supplied to the droplet surfaces to compensate for heat absorption at evaporation, whereas mass transfer is inessential. This case is specific to fast evaporation in a hot gaseous mixture whose temperature is sufficiently close or even exceeds the liquid boiling point. It pertains to a number of industrial situations frequently encountered in power engineering, such as evaporative cooling of gases.

3.1. Slow diffusion-controlled evaporation

If the mean temperature of the gaseous mixture that contains evaporating droplets is low enough, the evaporation is slow, and its thermal effect can be ignored. Consequently, the kinetics of evaporation of individual droplets is determined by the transport of vapour away from the droplet surfaces. Furthermore, if the droplet radii considerably exceed the mean free path length of molecules in the ambient gas, this transport can be described as a diffusion process. Under conditions of ideal mixing, there are then only one parameter that determines the state of a droplet - its radius $\xi = r$, and the only relevant variable characteristic of the current state of the gaseous mixture - the mean vapour concentration, $c(t)$, in the bulk.

We make use of this comparatively unsophisticated evaporation process that proceeds under ideal mixing conditions in order to demonstrate, in rather a meticulous way, different possible approaches to treating the evolution of a particulate system.

Equation (2) can now be specified as follows

$$w = \frac{dr}{dt} = -M(t)R(t),\ M = \frac{D}{\rho}\left[c^*(t) - c(t)\right],\ N = \frac{1}{r}, \tag{15}$$

where $c^*(t)$ is the equilibrium vapour concentration, D is the vapour diffusivity, and ρ is the liquid density. For the case of evaporation, we have $c < c^*$, and $w < 0$, while the inverted inequalities conform to condensation. Equation (3) has to be formulated as

$$\frac{dc}{dt} = -\rho \int_0^\infty f(t,r)\left(4\pi r^2 \frac{dr}{dt}\right) dr \tag{16}$$

and it describes the material balance as is maintained in the system under study in a differential form. It can be replaced right away by an equation that reflects the integral material balance

$$c(t) + \frac{4\pi}{3}\rho \int_0^\infty f(t,r) r^3 dr = c_0 + \frac{4\pi}{3}\rho n_0 \langle r^3 \rangle_0, \tag{17}$$

where subscript 0 referring to the initial state, n being the number concentration of droplets, and angular brackets signifying integration over r with a weight function of $f(t,r)$.

Equation (17) is supposed to be a result of integration of differential material balance equation (16). However, the relation between equations (16) and (17) is not strictly evident, and it needs some comments. Differentiation of the last equation with respect to time formally yields an equation

$$\frac{dc}{dt} = -\frac{4\pi}{3}\rho \int\limits_0^\infty \frac{\partial f}{\partial t} r^3 dr$$

because the variable of integration, r, must not of course be differentiated. With the aid of kinetic equation (1), this equation can be transformed to give, in succession,

$$-\int\limits_0^\infty \frac{\partial f}{\partial t} r^3 dr = \int\limits_0^\infty \frac{\partial}{\partial r}\left(\frac{dr}{dt} f\right) r^3 dr = \frac{dr}{dt} f(t,r) r^3 \Big|_{r=0}^{\infty} - 3\int\limits_0^\infty f(t,r)\left(r^2 \frac{dr}{dt}\right) dr.$$

Thus, we recover equation (16) when the first term in the right-hand side turns to zero, which happens if the particle population density 1) tends to zero faster than $1/r^2$ as r goes to infinity, and 2) diverges at $r \to 0$ slower than $1/r^2$. Apart from other things, this simple consideration shows that one should be rather careful while dealing with distribution functions.

Equation (11) reduces in the case under study to the following form

$$R(r;s) = 2Csr \exp\left(-sr^2\right), \tag{18}$$

where a factor of s having been added to the constant coefficient in this equation. We shall start with addressing the simplest case where the initial population density can be approximated with sufficient accuracy by function (18) with a certain fixed s.

Instead of using formal expression (12) for $F(t;s)$, we come back to the first equation (6) and to condition (10) that read, with allowance made for equation (15),

$$\frac{dF}{dt} + \frac{2D}{\rho} s\left[c^*(t) - c(t)\right] F = 0,\ F(0) = 1. \tag{19}$$

Using representation (5) of the wanted solution, we have from equation (17)

$$c(t) = c_0 + \frac{4\pi}{3}\rho n_0 \langle r^3\rangle_0 \left[1 - F(t;s)\right] \tag{20}$$

whence, after inserting this in equation (19), we obtain

$$\begin{aligned} &\frac{dF}{dt} + a(t)F + bF^2 = 0,\ a(t) = \frac{2D}{\rho}\left[c^*(t) - c_0 - \frac{4\pi}{3}\rho n_0 \langle r^3\rangle_0\right] s, \\ &b = \frac{8\pi}{3} D n_0 \langle r^3\rangle_0 s,\ n_0 = \int\limits_0^\infty f(0;r)dr = \int\limits_0^\infty R(r;s)dr = C. \end{aligned} \tag{21}$$

When deriving this equation, the self-similarity property of the population density $f = FR$ with R defined by equation (18) has been accounted of, according to which moments of $f(t,r)$ remain invariable during the evolution process. In particular, the third moment equals

$$\langle r^3\rangle = \frac{1}{n(t)} \int\limits_0^\infty f(t,r) r^3 dr = \langle r^3\rangle_0 = \frac{1}{n_0} \int\limits_0^\infty f(0;r) r^3 dr = \frac{3\sqrt{\pi}}{4s^{3/2}} \tag{22}$$

as can be easily seen from the above relations.

It is not difficult to solve equation (21) at an arbitrary dependence of c^* on t which might be dictated by the thermal regime of evaporation. If true isothermal conditions are maintained in the sense that $c^* = 0$, a is also independent of time, and we readily obtain from equation (21)

$$F(t;s) = \left[\left(1+\frac{b}{a}\right)\exp(at) - \frac{b}{a}\right]^{-1} \approx \left(1+\frac{b}{a}\right)\exp(-at) \tag{23}$$

an approximate equality holding true at sufficiently large times, that is, at $at \gg 1$. The particle population distribution density and the number concentration of droplets can be presented in an exceedingly simple form, approximate equalities being again valid at large times,

$$\begin{aligned} f(t,r) &= 2sn_0F(t;s)\exp\left(-sr^2\right) \approx 2\left(1+\frac{b}{a}\right)sn_0r\exp\left(-at-sr^2\right), \\ n(t) &= n_0F(t) \approx \left(1+\frac{b}{a}\right)n_0e\exp(-at), \ s \equiv \left(\frac{4}{3\sqrt{\pi}}\langle r^3\rangle_0\right)^{2/3}. \end{aligned} \tag{24}$$

It is worthwhile to stress once again that population distribution density (24) is self-similar in the sense that the droplet assemblage evolution affects merely the total number of droplets which eventually disappear during the process, but not the distribution moments of any order.

In a more general case, the initial population density cannot be represented by function (18). Notwithstanding, it can be sometimes described with a good accuracy as a sum of a few elementary self-similar functions of the type of that in equation (18), that is,

$$f(0,r) = 2\sum_{j=1}^{J} C_j s_j r\exp\left(-s_jr^2\right), \ \sum_{j=1}^{J} C_j \equiv n_0. \tag{25}$$

In order to obtain $f(t,r)$, each elementary function $R(t;s_j) = 2C_js_jr\exp(-s_jr^2)$ that appears in this equation must be multiplied by a proper $F(t;s_j)$, and then the products have to be summed up, according definition (5) and quite similarly to equation (25). The problem of calculating $F(t;s_j)$ is essentially the same as before, and it is formulated in equation (19) where s_j substitutes for s. The resultant equations for different $F(t;s_j)$ lead at once to the following relations

$$s_j\ln F_j = s_j\ln F_i, \text{ and } F_j^{s_i} = F_i^{s_j}, \ F_j \equiv F(t;s_j) \tag{26}$$

valid for any couple of integers i and j that may vary from unity to J.

Equation (26) proves that only a single function among $F(t;s_j)$ must be found to determine all of them. For the sake of definiteness, we arrange the set of s_j in such a manner that $s_j > s_i$ at $j > i$, and we also choose $F_1(t) \equiv F(t;s_1)$ to be determined first. After a simple manipulation, which is in essence precisely the same as that has led to equation (21), we arrive at a new problem

$$\begin{aligned} &\frac{dF_1}{dt} + \left(a_1(t) + \sum_{j=1}^{J} b_jF_1^{s_j/s_1}\right)F_1 = 0, \ F_1(0) = 1, \\ &a_1(t) = \frac{2D}{\rho}\left[c^*(t) - c_0 - \pi^{3/2}\rho\sum_{j=1}^{J}\frac{C_j}{s_j^{3/2}}\right]s_1, \ b_j = \frac{2\pi^{3/2}DC_j}{s_j^{3/2}}s_1. \end{aligned} \tag{27}$$

This equation can always be integrated numerically. Besides, if c^* is constant, and $s_j = k_js_1$, where k_j are integral numbers, the right-hand side of this equation represents a polynomial. After expanding this polynomial into elementary multipliers, equation (27) can be integrated analytically to yield an algebraic transcendental equation that relates F_1 to t in an implicit form.

The population size distribution density is expressible in the case under consideration as

$$f(t;r) = 2\sum_{j=1}^{J} C_j s_j F_1^{s_j/s_1}(t) r \exp\left(-s_j r^2\right). \tag{28}$$

Equation (28) permits a straightforward evaluation of different characteristics of the droplet assemblage. For instance, we have for the droplet number concentration and for the third distribution moment that determines the mean droplet volume as functions of time

$$\begin{aligned} n(t) &= \sum_{j=1}^{J} C_j F_1^{s_j/s_1}(t) \to C_1 F_1(t),\ t \to \infty, \\ \langle r^3 \rangle(t) &= \frac{3\sqrt{\pi}}{4n(t)} \sum_{j=1}^{J} \frac{C_j}{s_j^{3/2}} F_1^{s_j/s_1}(t) \to \frac{3\sqrt{\pi}}{4s_1^{3/2}},\ t \to \infty, \end{aligned} \tag{29}$$

which agrees asymptotically with equation (22). The bulk vapour concentration can now be found from equations (17) and (29)

$$c(t) = c_0 + \pi^{3/2}\rho \sum_{j=1}^{J} \frac{C_j}{s_j^{3/2}} \left[1 - F_1^{s_j/s_1}(t)\right]. \tag{30}$$

Because of the obvious inequality $F_1 < 0$ at $t > 0$, it can be clearly seen that the first term of sum (28) becomes to dominate as time grows, no matter how insignificant it might be at $t = 0$, and how large coefficients C_j have been assigned to describe the other terms of this sum at the initial moment. More generally, only the influence of that part of the initial distribution that is described by function (18) with $s = s_1$, that is, with the smallest s_j, persists to cause a noticeable effect on droplet assemblage properties after sufficiently long time intervals, as it is shown in equation (30). In other words, after a period of time, the system forgets particulars of its initial state, and consequently, a final self-similar evolution stage virtually establishes itself. It is not difficult to see that the original maxima of the population size distribution density attained at smaller values of r degenerate faster than those corresponding to larger r. This also means that any moment $\langle r^m \rangle$ of this distribution must increase with time due to the assemblage evaporation, until the self-similar stage is attained where any moment becomes approximately invariable.

At last, we turn to the case where the initial size distribution density is described by an arbitrary continuous function, $f(0,r) = f_0(r)$. In this case, the very form of self-similar distributions (18) suggests looking for the particle population distribution density, $f(t,r)$, as an integral transformation with a kernel belonging to the same class as function (18). Therefore, we take

$$f(t,r) = r\int_0^\infty A(s) F(t;s) \exp\left(-sr^2\right) ds \tag{31}$$

and, after accepting that $F(0;s) = 1$ in compliance with equations (19) and (27), we also obtain

$$f_0(r) = f(0,r) = r\int_0^\infty A(s) \exp\left(-sr^2\right) ds. \tag{32}$$

Our immediate task consists in determining function $A(s)$ that is involved in these equations, in terms of the initial size distribution that is presumed given. With the introduction of a new

independent variable, $z = r^2$, we become able to rewrite equation (32) in a familiar form of Laplace transformation, that is,

$$g(z) \equiv \left.\frac{f_0(r)}{r}\right|_{r=\sqrt{z}} = \int_0^\infty A(s) \exp(-sz)\, ds. \tag{33}$$

This equation allows us to regard function $A(s)$ as the inverse Laplace transform of the known function, $g(z)$, that is defined in terms of the initial distribution. Couples of functions connected by the Laplace transform are well tabulated, so that $A(s)$ can be found for a great many $f_0(t)$ without need to undertake any calculation.

It seems natural, when using an analogy with equation (26), to take $F(t;s) = F^s(t)$ where $F(t)$ is a new unknown variable. In this case, after simple transformations that are similar to those employed above, we come out with a problem

$$\frac{dF}{dt} + \left(\frac{a(t)}{s} + \pi^{3/2} D \int_0^\infty A(s) F^s \exp\left(-sr^2\right) \frac{ds}{s^{5/2}} \right) F = 0,\ F(0) = 1, \tag{34}$$

where ratio $a(t)/s$ is independent of s, with $a(t)$ being defined in accordance with equation (21). In contrast to equations (21) and (27), this equation is an integro-differential. Function $F(t)$ found as a solution to problem (34) finally determines the particle size distribution density in accordance with equation (31). However, the handling of this integro-differential equation seems to be somewhat easier than either analytical or numerical analysis of conventional integro-differential equation that can be immediately obtained from equations (1) and (17), when supplemented with equation (15). Below, we briefly demonstrate the derivation of this equation for reference sake.

Applying the well-known method of characteristics to equations (1) and (15), one obtains

$$f(t,r) = \frac{r}{\left[r^2 + \theta(t)\right]^{1/2}} f_0\left(\left[r^2 + \theta(t)\right]^{1/2} \right),\ \theta(t) = \frac{2D}{\rho} \int_0^t \left[c^*(t) - c(t)\right] dt.$$

Substituting this into equation (17), one arrives further at a rather complicated integro-differential equation for function $\theta(t)$ which we do not attempt to write down here. The bulk vapour concentration is related to the unknown variable of this equation, $\theta(t)$,

$$c(t) = c^*(t) - \frac{\rho}{2D} \frac{d\theta}{dt}.$$

In the generalized case, solving the last integro-differential equation is hardly an easier task than applying conventional methods directly to the kinetic equation. These time-consuming conventional methods are usually based on either dividing the assemblage into separate fractions, or analyzing moments of the population size distribution density. Being much simpler, the calculation scheme developed above possesses certain evident advantages over schemes resulting from these methods. In particular, it can readily be used for the express evaluation of various significant characteristics of an evolving particulate system, and it can be simplified even more.

The further simplification becomes possible due to the fact that the time necessary for the final self-similar evolution stage to establish itself often happens to be much shorter than the duration of the evolution process of a particulate system being considered. Consequently, it is this self-similar stage that frequently governs the process at large, and approximately determines the time dependence of different system's characteristics. This is a rather fortunate occurrence, since the

population size distribution density is then most advantageously described by exceedingly simple equation of the type of (24), whereas mean properties of the ambient medium can be found from equations of the type of equation (20) for vapour concentration.

Among important characteristics of particulate systems, the "degree of transformation"

$$y(t) = \frac{n(t)\langle r^3\rangle(t)}{n_0\langle r^3\rangle_0} \tag{35}$$

seems to be of special practical concern. At the self-similar stage, the third distribution moment does not depend on time, and the degree of transformation equals $F(t)$ as defined by equation (21) for the particular case of slow diffusion-controlled evaporation just considered. In this particular case, $y(t)$ is the fraction of liquid that remains in the form of droplets by moment t, and at the same time, it coincides with the fraction of the total number of droplets that have not evaporated by the moment indicated. In other situations, the degree of transformation can of course have a different physical meaning.

3.2. Fast thermally-controlled evaporation

Absorption of heat by evaporating droplets influences the kinetics of evaporation as well. Allowance for this influence implies 1) an appropriate correction to be introduced to formula (15) for the evaporation rate of a single droplet that would account for the effect caused by thermal factors, and 2) a heat balance equation to be considered alongside material balance equation (16) or (17). However, the said influence is practically insignificant, if the mean system temperature, T, remains well below the liquid saturation temperature, T_s. However, the situation drastically changes as T approaches, or even becomes larger than T_s. If this is the case, it is the heat transfer to the droplet surfaces that limit the evaporation rate of individual droplets, and the resistance due to diffusion of vapour from these surfaces may be regarded as negligible. We again consider the evaporation process at conditions of ideal mixing.

There are theoretical and empirical formulae for the rate of evaporation of a single droplet in the thermally-controlled regime. For definiteness, we make use of one of available empirical expressions for this rate that leads to the formula

$$w = \frac{dr}{dt} = -M(t)R(r),\ M = \frac{k}{\rho L}\langle r\rangle_0^m\,(T - T_s)\,,\ N = \frac{1}{r^m}, \tag{36}$$

where k is a constant that plays the role of an effective heat exchange coefficient, and m is a constant exponent. Formula (36) is valid in cases where the actual system temperature is larger than the saturation temperature, or the liquid boiling point, T_s. Equation (16) has now be replaced by the heat balance equation

$$c_p\frac{dT}{dt} = \mu L\frac{dy}{dt},\ c_p = c_g + \mu(1-y)c_v. \tag{37}$$

Here, μ is the ratio of an initial mass of the droplets to the mass of gas, and c_p is the isobaric heat capacity of the gas-vapour mixture expressed in terms of the specific heat capacities of the gas and vapour, c_g and c_v, respectively. Function $y = y(t)$ stands for the degree of transformation as defined by equation (35). Equation (37) establishes the fact that heat delivered to the droplets from the mixture is spent entirely on evaporation. For simplicity, the mixture pressure is assumed invariable, so that the saturation temperature is constant.

The self-similar population size distribution density is once again looked for in the form

$$f(t,r) = F(t)R(r),\ F(t) \equiv y(t). \tag{38}$$

The problem for $R(r)$ reads

$$\frac{d}{dr}\left(\frac{R}{r^m}\right) + s(m+1)R = 0,\ \int\limits_0^\infty R(r)dr = 0, \tag{39}$$

$s(m+1)$ being a separation constant, and its solution can be written out as

$$R(r) = n_0 s(m+1) r^m \exp\left(-sr^{m+1}\right),\ s = \Gamma^{m+1}\left(\frac{m+2}{m+1}\right)\langle r\rangle_0^{-(m+1)}, \tag{40}$$

$\Gamma(x)$ being the Eulerian gamma-function. The problem for function $F(t)$ is

$$\frac{dF}{dt} + \lambda\vartheta F = 0,\ F(0) = 1,\ \vartheta \equiv T - T_s,\ \lambda = \frac{(m+1)k}{\rho L}\langle r\rangle_0^m s. \tag{41}$$

A trouble with this problem consists in the fact that the current temperature difference depends on time implicitly, through the degree of transformation $y(t) = F(t)$, as it is evidenced by equation (37). However, the said equation can be readily integrated to yield

$$\vartheta = \vartheta_0 - \frac{L}{c_v}\ln\frac{c_g + \mu(1-y)c_v}{c_g},\ \vartheta \equiv T_0 - T, \tag{42}$$

T_0 being an initial system temperature. Equations (41) and (42) lead to a problem for $y(t)$

$$\frac{dy}{dt} + \lambda\left[\vartheta_0 - \frac{L}{c_v}\ln\frac{c_g + \mu(1-y)c_v}{c_g}\right]y = 0,\ y(0) = 1. \tag{43}$$

It is not difficult to integrate this equation numerically. However, a sufficiently accurate solution to problem (43) can be obtained by expanding the logarithmic term into a Taylor series and by retaining only the terms up to the second order inclusive. As a result, we obtain

$$\frac{dy}{dt} + ay + by^2 = 0,\ y(0) = 1,\ a = \lambda\left(\vartheta_0 - \vartheta^*\right),\ b = \lambda\vartheta^*,\ \vartheta^* = \frac{\mu L}{c_g}. \tag{44}$$

The wanted solution to this problem coincides with the presented in equation (23). Allowing for the new definition of a and b in equation (44), we rewrite it as follows

$$y(t) = \frac{\vartheta_0 - \vartheta^*}{\vartheta_0\exp\left[\lambda\left(\vartheta_0 - \vartheta^*\right)t\right] - \vartheta^*}. \tag{45}$$

Hence we derive an approximate solution that is valid at long times

$$y(t) \approx \left(1 - \frac{\vartheta^*}{\vartheta_0}\right)\exp\left[-\lambda\left(\vartheta_0 - \vartheta^*\right)t\right],\ t \gg \frac{1}{\lambda\left(\vartheta_0 - \vartheta^*\right)},\ \vartheta_0 > \vartheta^*. \tag{46}$$

Equation (46) is formulated for the case when initial mixture temperature T_0 is high enough to ensure complete evaporation of all the droplets that where present in the system at the initial moment. In the opposite case, the mixture attains a thermodynamic equilibrium state at $t \to \infty$, and equilibrium state is characterized by a relation that follows directly from equation (45)

$$y_\infty = 1 - \frac{\vartheta_0}{\vartheta^*},\ \vartheta_0 < \vartheta^*. \tag{47}$$

In a special case where the initial superheat or the two-phase mixture is just sufficient to evaporate all suspended droplets, equation (46) must be replaced by

$$y(t) = \frac{1}{1 + \lambda \vartheta_0 t}, \ \vartheta_0 = \vartheta^*. \tag{48}$$

Inserting the degree of transformation from equation (45) into equation (37) leads to a new equation that describes the temperature variation in the evaporation process

$$\vartheta \frac{d^2\vartheta}{dt^2} - \left(\frac{d\vartheta}{dt}\right)^2 + \lambda \vartheta^2 \frac{d\vartheta}{dt} = 0, \ \vartheta(0) = \vartheta_0 \tag{49}$$

the solution of which reads as follows

$$\vartheta(t) = \vartheta_0 \left(1 - \frac{\vartheta^*}{\vartheta_0}\right) \left\{1 - \frac{\vartheta^*}{\vartheta_0} \exp\left[-\lambda \left(\vartheta_0 - \vartheta^*\right) t\right]\right\}^{-1}. \tag{50}$$

Analytical results derived in this section have been checked by comparing them with experimental data reported by different authors, and agreement was always satisfactory.

4. Dissolution of dispersed solids

Another example of particulate processes to which the method developed can be most advantageously applied concerns various technological schemes which involve dissolution of a polydisperse assemblage of particles in a liquid mixture. The dissolution processes are even somewhat simpler to treat than evaporation processes that have been addressed in the preceding section, since the dependence of the transformation rate for a single particle can be usually described with the help of less sophisticated relations. In particular, if particles dissolve in a well-stirred tank, the ideal mixing approximation applies again. If mixing is vigorous enough, the dissolution rate of a single particle often happens to be independent of particle size [5–9], and it can be expressed by the following formula

$$w = \frac{dr}{dt} = -M(t)N(r), \ M = \frac{k}{\rho}\left[c^*(t) - c(t)\right], \ N = 1, \tag{51}$$

where k now designates a constant mass transfer coefficient, ρ is now the particle material density, and c and c^* are the mean concentration of the solute and its equilibrium value at the saturation conditions, respectively. In the case under consideration, this formula substitutes for the previously employed kinetics expressed by equations (15) and (36). It holds true under conditions of co-current two-phase mixture flow, as well as in mixer-type apparatuses in which there is a periodic external supply of solids and withdrawal of solution. In both the cases mentioned, the mass balance equation that replaces equation (17) can be formulated as

$$c(t) = c_0 + \beta_0 \left[1 - y(t)\right], \tag{52}$$

where c_0 is an initial solute concentration, β_0 is an initial mass of solids within a unit mixture volume, and $y(t)$ is the transformation rate as identified in equation (35).

When dropping out particulars of the calculation, which strongly resembles those in the preceding section, but are actually even simpler, we present an expression for the self-similar population density that substitutes for equations (18) or (40)

$$R(r) = n_0 s \exp\left(-sr\right), \ s = \langle r \rangle_0^{-1} \tag{53}$$

and states that unknown variable $F(t) = y(t)$ again satisfies an equation of the type of (43), with coefficients

$$a(t) = \frac{k}{\rho}\left[c^*(t) - c_0 - \beta_0\right] s,\ b = \frac{k\beta_0}{\rho} s. \tag{54}$$

In a particular case (say, under isothermal and isobaric conditions), where the equilibrium concentration does not depend on time, the wanted solution is given by equation (23), and it can be conveniently rewritten in the form

$$y(t) = \left[\frac{\exp(\lambda t)}{1-\alpha} + \frac{1}{\alpha}\right]^{-1} \approx (1-\alpha)\exp(-\lambda t),\ t \gg \frac{1}{\lambda};\ \alpha = \frac{c^* - c_0}{\beta_0},\ \lambda = \frac{k}{\rho}(1-\alpha)\langle r\rangle_0^{-1}. \tag{55}$$

Under conditions of counter-current flow, equations (51) and (52) give way to

$$M = -\frac{k}{\rho}\left[c^*(t) - c_0 - \beta_0 y(t)\right],\ N = 1,\ c(t) = c_0 + \beta_0 y(t). \tag{56}$$

A similar analysis results now in the same equation (55) for the degree of transformation, but with coefficient λ being now specified as $\lambda = (k/\rho)\alpha\langle r\rangle_0^{-1}$, and this is the only substantial difference between dissolution in well mixed co- and counter-current turbulent flows.

The analytical formulae listed that pertain to self-similar processes were used to correlate different experimental data, and the resultant correlations were surprisingly good.

5. Conclusions

The theory developed here can be advantageously applied in studies involving different physical processes. So, for instance, combustion of dispersed fuels and phase transitions in supercooled (supersaturated) liquids may be mentioned.

It is well-known that there exists a very wide variety of combustion processes of polydisperse, either liquid or solid, fuels which are extremely popular in everyday life and different fields of industry. These processes are effected in multifarious furnaces and other devices of different origin and design, ranging from relatively primitive ovens and boilers, through various sophisticated furnaces of modern power plants, to combustion chambers of rocket propellants [10,11]. Due to a great diversity of fuel physical state and chemical composition, as well as to an exceedingly broad range of possible operating conditions, the kinetics of these processes can be governed by quite different physical and chemical transformations. As a result, there are great many regime-dependent relations that describe the rate of burning of a single particle under different thermal and flow conditions [12,13].

Another example consists in investigating the bulk formation of the new phase in the supercooled (supersaturated) layer upstream of the phase transition front at the stage of simultaneous nucleation and growth of the solid phase elements. Still now, no systematic study of this phenomenon was performed because no generalized methods were detailed for investigating the initial, intermediate and concluding stages of this phase transition process as a whole. A number of recent successful attempts in this way devoting to a theoretical description of the aforementioned stages (nucleation [14–19], instability of the solid-liquid phase interface [20–24], dendritic growth [25–29] and mushy layer evolution [30–38]) may be mentioned.

The present paper shows that analytic investigation of a number of major processes and factors in the theory of evolution of particulate systems involves fundamental difficulties and requires the use of qualitatively new approaches and concepts. These aspects also require detailed work in future studies.

6. References

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